

THE 1994 NORTHERN MIDLATITUDE BUDGET OF STRATOSPHERIC CHLORINE DERIVED FROM ATMOS/ATLAS-3 OBSERVATIONS

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Abstract Volume mixing ratio (VMR) profiles of the chlorine-bearing gases HCl, ClONO₂, CCl₃F, CCl₂F₂, CHCl₃, CCl₄, and CH₃Cl have been measured between 3 and 49° northern- and 65 to 72° southern latitudes with the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument during the Atmospheric Laboratory for Applications and Science (ATLAS)-3 shuttle mission of 3 to 12 November 1994. A subset of these profiles obtained between 20 and 49°N at sunset, combined with ClO profiles measured by the Millimeter-wave Atmospheric Sounder (MAS) also from aboard ATLAS-3, and measurements by balloon for HOCl, CH₃CCl₃ and C₂Cl₃F₃, indicate that the mean burden of chlorine, Cl_{bur}, was equal to (3.50 ± 0.15)

ppbv (parts per billion by volume, or $\times 10^{-9}$), 1-sigma, throughout the stratosphere. at the time of the ATLAS3 mission. This is some. 36% larger than the mean **2.58** ppbv value measured by ATMOS within the same latitude zone during the Spacelab3 flight of 29 April to 6 May 1985, consistent with an exponential growth rate of the chlorine loading in the stratosphere equal to 3.2 %/yr or a linear increase of 0.10 ppbv/yr over the Spring-1985 to Fall-1994 time period. These findings are in agreement with both the burden and increase of the main anthropogenic Cl-bearing source gases at the surface during the 1980s, confirming that the stratospheric chlorine loading is primarily of anthropogenic origin.

INTRODUCTION

The Atmosphere Trace Molecule (ATMOS) experiment is a multi-mission, shuttle-based project designed for regular, detailed remote soundings of the Earth's middle atmosphere [Farmer, 1987; Gunson, 1992; Gunson et al., 1996].

During its mission of 1985, ATMOS demonstrated, for the first time, the capability of establishing the budget of and partitioning among the nitrogen, chlorine and fluorine "families" [Russell et al., 1988; Zander et al., 1992] through infrared remote sensing from space. Subsequently, ATMOS was selected as a core instrument of the ATLAS program, performing additional missions in 1992, 1993 and 1994 [Gunson et al., 1996].

In this letter, we report volume mixing ratio profiles for the 7 most important Cl-bearing gases derived from a subset of ATMOS/ATLAS-3 sunset occultations observed at northern latitudes comparable to those covered during ATMOS/Spacelab-3 in 1985. By complementing these with profiles of 4 additional, non-negligible chlorinated species measured by other experiments, we evaluate the 1994 stratospheric chlorine budget and derive its rate of change over the 1985 to 1994 time period.

DATABASE AND ANALYSIS

The main absorption features used for VMR retrievals of the chlorine-bearing target molecules observed by ATMOS are primarily those reported in Table 1 of Zander et al. [1992]. This involves analyzing the ATMOS observations with the filters #12 (600-1400 cm^{-1}), #9 (600-2450 cm^{-1}) and #3 (1580 - 342.0 cm^{-1}) which were used alternately during the ATLAS-3 mission in predetermined sequences during 68

sunset occultations that occurred between 20 and 49°N; among these, a few were discarded for altitude coverage incompleteness (missing or poor quality individual spectra) so that the present study encompasses 22 filter 12, 11 filter 9 and 28 filter 3 occultations. In order to evaluate the latitudinal dependence of the VMR profiles, we subdivided the 20 to 49°N range of latitudes into "midlatitude" (49 to 35°N) and "subtropical" (35 to 20°N) zones. The molecules HCl and CH₃Cl are studied in filter 3 occultations, while all other ATMOS-retrieved gases are obtained from filter 9 and 12 events; to eliminate any biasing arising from the sampling of the different ensembles of the filter 3 or the filter 9 and 12 occultations, we used N₂O as a dynamical tracer to register HCl and CH₃Cl profiles on the same vertical scale as the other gas profiles.

The VMR profiles were retrieved with the ODS (Occultation Display Spectra) code, an onion-peeling retrieval algorithm developed at JPL and described by Norton and Rinsland [1991]. The input data to the code and parameters necessary to retrieve consistent composition of the atmosphere are discussed by Gunson et al. [1996].

The adoption of absorption cross-sections for a number of heavy molecules such as CCl₂F₂, CCl₃F, Cl₂CO, ClONO₂,..., which progressively superseded "fudged", pseudo-line parameters [Zander et al., 1987; Brown et al., 1987] greatly improved the absolute quality of related ATMOS data retrievals reported here [Brown et al., 1996].

RESULTS

The mean HCl VMR (volume mixing ratio) value obtained by averaging all individual measurements made during the ATLAS-3 mission near and above 50 km altitude, and over the 3 to 49°N latitude zone was found equal to (3.50 ± 0.15) ppbv. Sub-binnings performed over the northern midlatitude and subtropical zones identified before indicated no statistically significant difference with respect to that mean, thus suggesting that HCl is well mixed at the hemispheric level near and above the stratopause; this was readily reported by Gunson et al. [1994] based on the analysis of ATMOS/ATLAS-1 observations in March-April 1992.

Two important conclusions emerged from the 1985 chlorine budget evaluation [Zander et al., 1992]. Firstly, it was found that, within the uncertainty of the measurements, the total chlorine burden (organic and inorganic combined) is preserved throughout the stratosphere. Secondly, the VMR measurement of HCl in

the vicinity of the stratopause (near 50 km altitude) is a good surrogate for total stratospheric chlorine loading, because (i) HCl is the only significant Cl-bearing sink observed there and above, (ii) all chlorinated reservoirs present at lower altitudes, in particular ClONO_2 , ClO , and HOCl , have negligible concentrations above about 45 km, and (iii) the main sources of Cl are almost entirely photodissociated above 40 km. Based on this conclusion, the northern latitude VMR of HCl near 50 km altitude made during the ATLAS-3 mission, i.e., (3.50 ± 0.15) ppbv, can be considered to represent the mean stratospheric loading of chlorine for the Fall-1994 time.

To corroborate this throughout the stratosphere, we evaluated the burden of chlorine, Cl_{TOT} , at various pressure levels by summing measured VMRS of the largest possible set of Cl-bearing gases (sources, sinks and reservoirs combined) weighted by the number of Cl atoms bound in each of them. For the ATLAS-3 time period, we performed the following summation:

$$\begin{aligned} \text{Cl}_{\text{TOT}} = & [\text{HCl}] + [\text{ClONO}_2] + 4 \times [\text{CCl}_4] + 3 \times [\text{CCl}_3\text{F}] + 2 \times [\text{CCl}_2\text{F}_2] \\ & + [\text{CHClF}_2] + [\text{CH}_3\text{Cl}] + \{\text{ClO}\} + 3 \times \{\text{CH}_3\text{CCl}_3\} + 3 \times \{\text{C}_2\text{Cl}_3\text{F}_3\} + \{\text{HOCl}\} \quad (1) \end{aligned}$$

where the brackets indicate the VMRs of the seven chlorinated constituents measured by ATMOS and the 4 braces refer to VMRs of additional, non-negligible chlorine contributors not retrieved by ATMOS but by other experiments. In particular, the ClO data were derived from the MAS (Millimeter-wave Atmospheric Sounder) experiment [Croskey et al., 1992] which was also part of the ATLAS-3 payload, so that these data are ideally suited for incorporation in the present chlorine budget investigation; details about the ClO data analysis have been reported by Aellig et al. [1996]. The VMR profiles for CH_3CCl_3 and $\text{C}_2\text{Cl}_3\text{F}_3$ were derived from in situ measurements during a balloon flight performed by the Jülich group (A. Engel, private communication) in Aire-sur-l'Adour, France, on 7 October 1994, i.e., about one month prior to the ATLAS-3 mission. The HOCl profile was obtained from the analysis of sunset spectra recorded with the Mark IV FTIR during a balloon flight in September 1993 near 32°N (G.C. Pion, private communication), scaled by a 3% increase per year to represent the HOCl loading at the time of the ATLAS-3 mission.

FIGURE 1 displays the profiles of the individual gases included in the present evaluation for both the, midlatitude (thin full lines) and the subtropical (thin dotted lines) zones, as well as the corresponding total Cl profiles labeled Cl_{TOT} displayed as thicker lines. For CH_3CCl_3 , $\text{C}_2\text{Cl}_3\text{F}_3$ and HOCl , the same profiles were used in both binnings, because of unavailable measurements for the two latitudinal zones.

TABLE 1 provides numerical VMR values for the northern midlatitude profiles displayed as full lines in Fig. 1, reported at a series of pressure levels consistent with the LJARS-pressure grid; these levels correspond to a slight oversampling when compared to the 3 to 4 km vertical resolution for the ATMOS/ATLAS-3 measurements, based on the finite instrument field-of-view.

The VMRs of the top and bottom pressure levels of the Cl_{TOT} profile are equal, respectively, to 3.52 and 3.71 ppbv, with a corresponding mean VMR and standard deviation over the entire altitude span equal to (3.51 ± 0.08) ppbv. The extremes are indicative of a 5.3% decrease of Cl_{TOT} which can be explained by the time delay for air to mix between 100 and 0.68 mbar (-16.5 to 50 km) levels.

The reported tangent heights (T.L.H.) in Table 1 are average values corresponding to the Filters 9 and 12 binnings.

FIGURE 2 with its linear abscissa scale shows some details of the profiles of the key components which make up the Cl inventory for the northern midlatitude case (35 to 490). In particular, we have reproduced the CCl_4 curve corresponding to the sum of Cl atom bound in all source gases reported in Table J. By further summing over CCl_4 and the inorganic compounds HCl , $ClONO_2$, ClO and $HOCl$ also reproduced in Fig. 2, one obtains the thicker continuous curve which corresponds to the total chlorine loading Cl_{TOT} . Within the estimated uncertainty ranging from 4% at the top to 6% at the bottom of the Cl_{TOT} profile, the conservation of chlorine is properly demonstrated throughout the stratosphere. Within that uncertainty, however, we can not rule out some missing, second order contributions in the 35 to 45 km and 18 to 28 km altitude layers caused by some combination of missing reservoirs (such as CO_2Cl_2 , ...) and sources (i.e., $C_2Cl_2F_4$, ...) not accounted for here. The lower altitude deficit could also reflect some uncertainty in the spectroscopic parameters used to derive the profiles of the heavier molecules involved in the present evaluation (for systematic error estimates in the spectroscopic parameters used in the inversion process, see Brown et al., 1996 and Gunson et al., 1996).

The evaluation of the Cl_{TOT} profile for the subtropical latitudinal zone (20-35°N; thick dotted line in Fig. 1) also indicates a decrease of over 5% between bottom (3.50 ppbv) and top (3.69 ppbv) VMRs, with a corresponding mean mixing ratio and standard deviation equal to (3.49 ± 0.11) ppbv; some deficit in the lower part of the profile is also noticed.

DISCUSSION AND CONCLUSIONS

The measurement of the budget of chlorine in the middle atmosphere involve a large number of Cl-bearing gases which can not be studied by any one technique alone, and related investigations during the last years have sought approaches for its evaluation, based on a more limited number of measurements. These have generally invoked the work of Plumb and Ko [1992] who demonstrated that there exist compact correlations between the mixing ratios of long-lived atmospheric constituents, thus providing means of deriving the distribution versus altitude for some species, solely based on concentrations measured for others. The procedure has been applied and formulated in many cases [e.g., Schmidt et al., 1994; Woodbridge et al., 1995]. Among these, the application by Schmidt et al. [1994] is of relevance here, as these authors demonstrated that there exist compact correlations between the mixing ratios of the most important, long-lived Cl-bearing source gases (which they sample routinely during multiple-species, in situ balloon soundings at mid- and high northern latitudes) and also between any one of these and the total organic chlorine, CCl_y , bound in all of those sampled. Using CCl_2F_2 as the "reference" source gas, Schmidt et al. [1994] derived the function

$$[\text{CCl}_y] = 0.045x [\text{CCl}_2\text{F}_2]^{1.82} + 67.35 \quad (2)$$

in which the brackets refer to the VMRS of the related compounds, expressed in units of ppt v ($\times 10^{-12}$ ppv). Application of the above formulation to the midlatitude mean CCl_2F_2 profile derived in 1994 by ATMOS produces results which match very well the CCl_y obtained in this work, when accounting for the fact that Schmidt et al. [1994] sample species accounting for 95% of the total organic chlorine. Worth being noted also is that the procedure proposed by Woodbridge et al. [1995], based on a correlation between N_2O and CCl_y , was applied by Rinsland et al. [1996] to derived values for CCl_y inside and outside of the Antarctic vortex, also based on ATMOS/ATLAS-3 observations; when combined with related measurements of HCl and ClONO_2 , Cl_{TOT} values equal to (3.48 ± 0.21) ppbv and (3.45 ± 0.24) ppbv are found, respectively outside and inside of the vortex, in excellent agreement with the present findings at northern midlatitudes.

Model evaluations of the chlorine partitioning in the stratosphere as reported here for the ATLAS-3 mission are dealt with and discussed by Michelsen et al. [1996].

From the various independent results derived here, it can be concluded that the overall chlorine loading at the top of the stratosphere over the 20 to 49°N latitudinal zone was equal to 3.50 ppbv at the time of the November 1994 ATLAS-3 mission, with a 1 sigma uncertainty of 0.15 ppbv or 4%; this uncertainty represents an estimated accuracy assessed as in previous investigations by Zander et al. [1990] and Gunson et al. [1990]. Throughout the stratosphere, the Cl_{TOT} VMR profiles combining the important sources sinks and reservoirs display consistent values which suggest some second order, local deficit and a slope reflecting the time for air to mix from the lower to the upper stratosphere.

When compared to the mean stratospheric chlorine VMR of 2.58 ± 0.10 ppbv derived from the 1985 ATMOS/Spacelab-3 mission [Zander et al., 1992], the present findings indicate an increase in the stratospheric chlorine loading equal to 36% over the 9.5 years time period separating the two missions. This is consistent with an increase corresponding to an exponential rate of 3.2%/yr or a linear change of 0.10 ppbv/yr. The mean stratospheric Cl VMR derived from the ATMOS/Spacelab-3 mission was shown to be in excellent agreement with the corresponding 1980 Cl inventory in the lower troposphere [Zander et al., 1992 and WMO Reports No. 16, 1986 and No. 18, 1990], indicative of a mixing time of about 5 years for free tropospheric air to be transported and mixed throughout the stratosphere. The upper stratospheric Cl loading derived here (3.50 ppbv) for the time of the ATLAS-3 mission of November 1994 mirrors precisely the tropospheric Cl content that prevailed in 1989-90 [WMO Reports No. 25, 1992 and No. 37, 1995], thus confirming the 4-5 year lag time between tropospheric and stratospheric chlorine loading identity (a similar delay has been reported by Bischof et al. [1985] and Schmidt and Khedim [1991], based on earlier measurements of the detailed distribution of CO_2 versus altitude). In addition, the rate of change, of 3.2 %/yr deduced here agrees very well with the increase of the organic chlorine burden in the lower troposphere (i.e., 0.104 ppbv for a total of 3.18 ppbv in 1986 and 0.109 ppbv for a total loading of 3.46 ppbv in 1989; see WMO Reports No. 18, 1989 and No. 25, 1992.; also NASA Pub. 1339, 1994).

As a consequence of the excellent agreement between the stratospheric chlorine loadings and rates of change derived from the ATMOS missions of 1985 and 1994 and the surface measurements of Cl-bearing gases some 4-5 years earlier, there remains little doubt that the bulk of stratospheric chlorine and its evolution are primarily associated with the release at the ground of chlorinated source gases produced industrially. As concluded by Gunson et al. [1994], this implies that natural sources of chlorine, in particular CH_3Cl and

perhaps CCl_4 , and volcanic activity, have contributed negligibly to the changes in the burden of Cl in the stratosphere over the last decade or so.

The 1987 Montreal Protocol and its London and Copenhagen Amendments are intended to reduce the future levels of atmospheric Chlorine (see continuous curves in **FIGURE 3, top frame**, adapted from Gunson et al. [1994]) by regulating the production and release in the atmosphere of the most important anthropogenic, Cl-bearing source gases at the ground, primarily the chlorofluorocarbons (CFCs). The successive ATMOS missions have provided thus far the most consistent and complete set of measurements (see the 4 HCl results displayed in Fig. 3) needed to "watch" the timely chlorine loading and to model its impact on ozone depletion throughout the entire stratosphere. Similar measurements will become critical in the near future when the stratospheric loading is expected to start decreasing, to test the implementation of the Protocol and the validity of the model predictions.

Also reproduced in Fig. 3 (bottom frame) is the model prediction in the surface fluorine loading during the recent and coming decades, based on F-bearing source gases emissions at the surface and atmospheric lifetimes [Prather and Watson, 1990]. "The increase in stratospheric F_2 has also been measured regularly by ATMOS (see the F_2 points in Fig. 3), and its burden and rate of change are in concordance with the HCl findings, suggesting that both gases are the ultimate sinks of chlorine and fluorine-bearing source gases released to the atmosphere from industrial production, and that background contributions from natural sources are negligible.

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FIGURE CAPTIONS

FIGURE 1.- Graphical representation of the individual volume mixing ratio profiles included in the evaluation of the 1994 stratospheric Cl-loading for the northern midlatitude (35 to 49°N; thin full lines) and subtropical (20 to 35°N; thin dashed lines) zones. The thicker full and dashed lines display the corresponding Cl budgets throughout the stratosphere, sources, sinks and reservoirs combined. Of the 11 reported profiles, 7 were derived from ATMOS/ATLAS-3 observations (non-braced molecules), 1 from MAS/ATLAS-3 (ClO) and 3 from balloon measurements (CH_3CCl_3 , $\text{C}_2\text{Cl}_3\text{F}_3$ and 1 IOCl). For details, see text. While all subtropical profiles experience uplifting, opposite relative contributions to Cl_{TOT} are noticeable between sources on one hand, and sinks and reservoirs on the other hand.

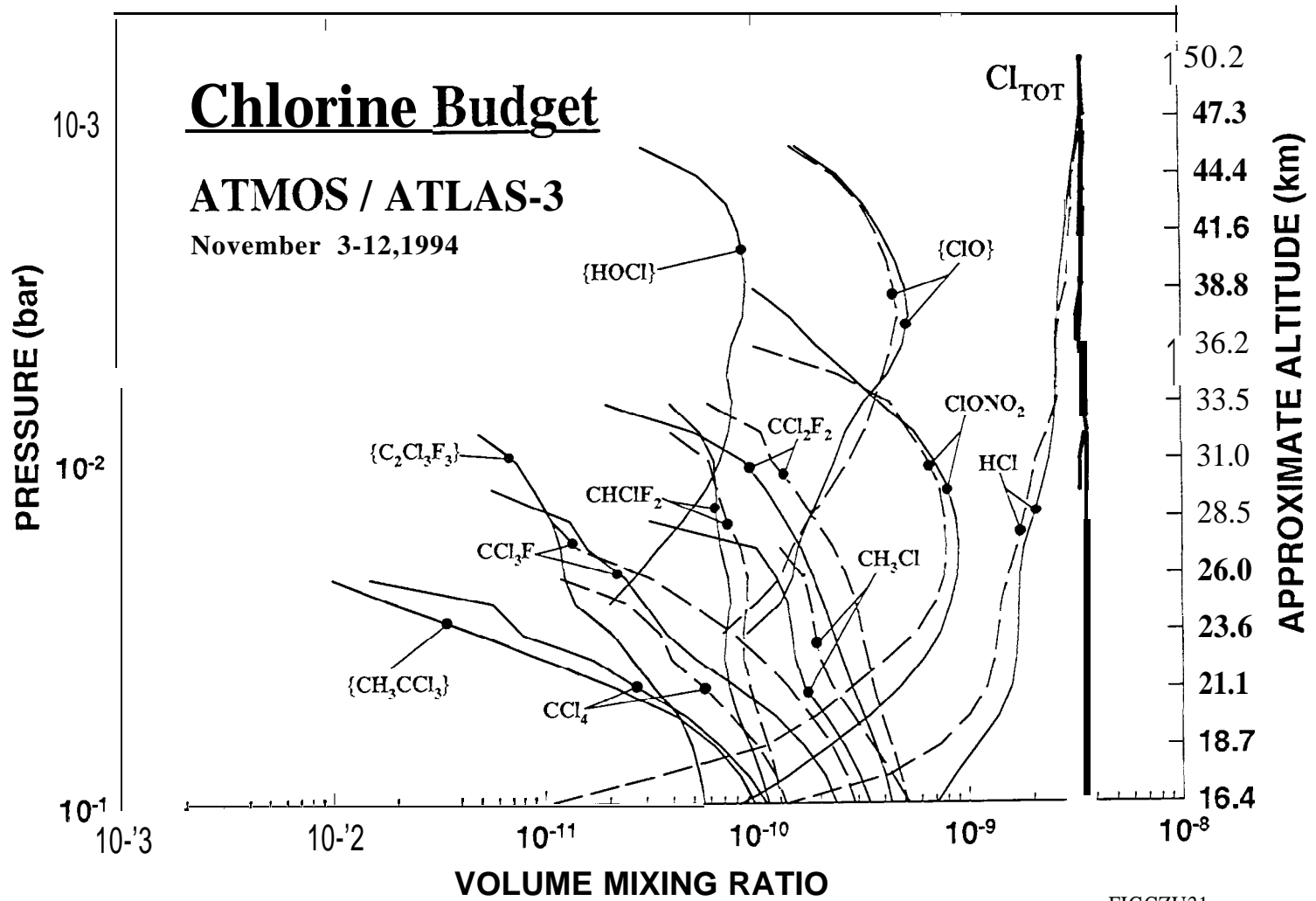
FIGURE 2.- A linear-scale presentation of the key components entering in the total Cl-loading evaluation throughout the stratosphere. The CCl_y curve refers to the total chlorine bound in all organic source gases listed in Table 1. Cl_{TOT} represents the summation over CCl_y , 1 HCl, ClONO_2 , ClO and HOCl.

FIGURE 3.- Representation of the modelled changes in total stratospheric chlorine and fluorine loading, based on the controlled release of long-lived Cl-bearing source gases by the Montreal Protocol and its Amendments. The 1985, 1992, 1993 and 1994 ATMOS measurements of HCl and CF_4 near the stratopause (~50 km), surrogates for the change in total stratospheric Cl and F loading, are reproduced by open circles; their offsets with respect to the model curve reflect the time for vertical transport and mixing from the ground up to the stratopause (as well as the contribution of CF_4 still present at 50 km altitude). The range of stratospheric chlorine and fluorine loading reflects the uncertainty in the future usage of chlorine and fluorine-bearing gases adopted as substitutes following the phase-out of the CFCs in 1996.

Table L- Northern Midlatitude Chlorine Budget through the stratosphere

P.,mbar T. H., km		HCl	ClONO ₂	CH ₃ Cl	CCl	CCl ₃ F	CCl ₂ F ₂	CHClF ₂	C ₂ Cl ₃ F ₃	CH ₃ CCl ₃	ClO	HOCl	Cl _{TOT}	CCl _y	N ₂ O
		all volume mixing ratios in 10 ⁻¹⁰ parts per volume													
0.68	50.15	35.20											35.20		36.4
1.00	47.25	34.30									0.50	0.10	34.90		51.7
1.47	44.36	31.50									2.50	0.72	34.72		68.4
2.15	41.55	29.30									4.00	0.85	34.15		117
3.16	38.82	27.20	1.21								5.20	0.92	34.53		228
4.64	36.15	26.40	1.73								5.10	0.79	34.02		379
6.81	33.54	26.10	3.89				0.20	0.40			3.30	0.79	34.88	0.80	560
10.00	30.99	24.10	6.92				0.88	0.63	0.08		2.40	0.68	36.71	2.61	819
14.68	28.48	20.20	8.84	0.32		0.13	1.37	0.66	0.11		1.80	0.46	35.75	4.45	1160
21.54	26.01	17.50	9.01	1.23	0.02	0.24	1.87	0.73	0.13	0.01	1.50	0.27	35.15	6.90	1400
31.62	23.58	17.10	7.46	1.48	0.08	0.36	2.31	0.73	0.21	0.05	0.90	0.15	34.62	9.01	1560
46.42	21.17	16.00	4.82	1.69	0.28	0.81	2.85	0.74	0.33	0.22		0.07	34.21	13.32	1870
68.13	18.78	11.00	2.22	2.60	0.67	1.68	3.63	0.92	0.49	0.63			35.09	21.87	2360
100.00	16.39	7.10	0.84	3.39	1.09	2.36	4.32	1.12	0.56	0.96			37.09	29.15	2780
Origin :		ATMOS	ATMOS	ATMOS	ATMOS	ATMOS	ATMOS	ATMOS	JÜLICH	JÜLICH	MAS	MkIV	All	All	ATMOS

TABLE 1



FIGCZU31

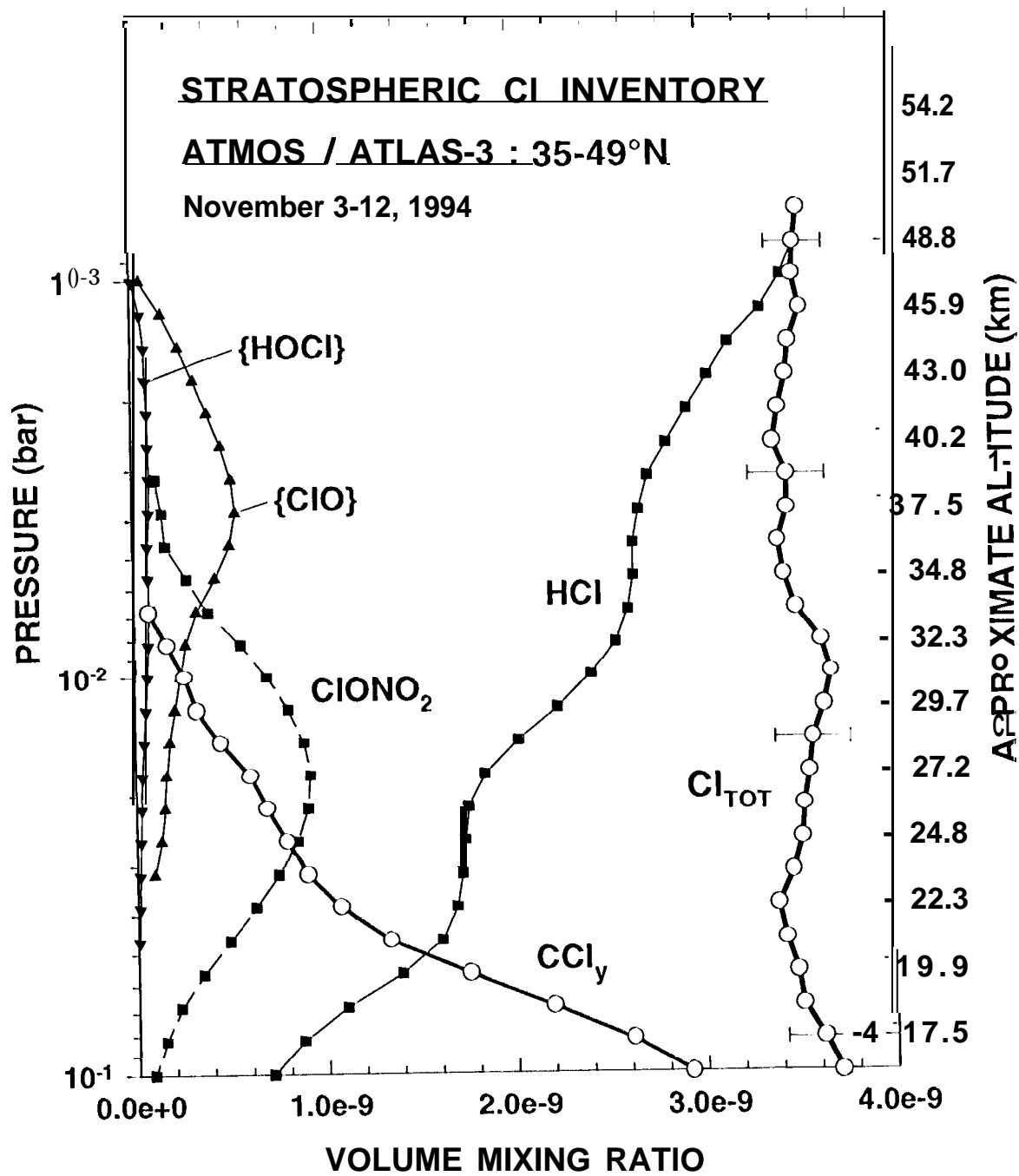


FIGURE 2

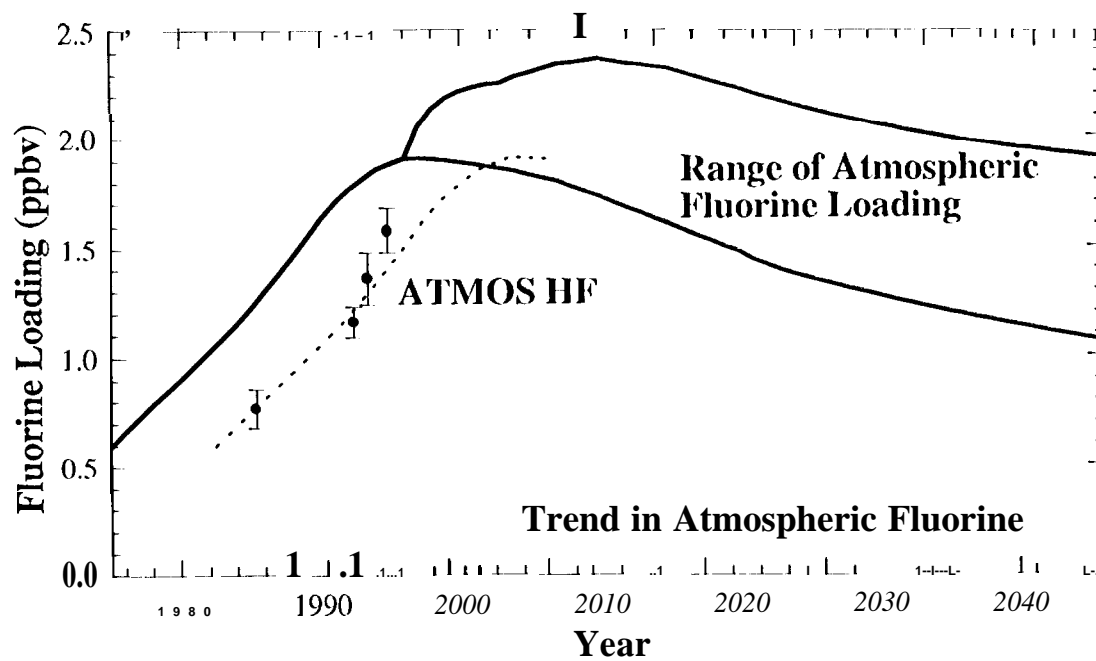
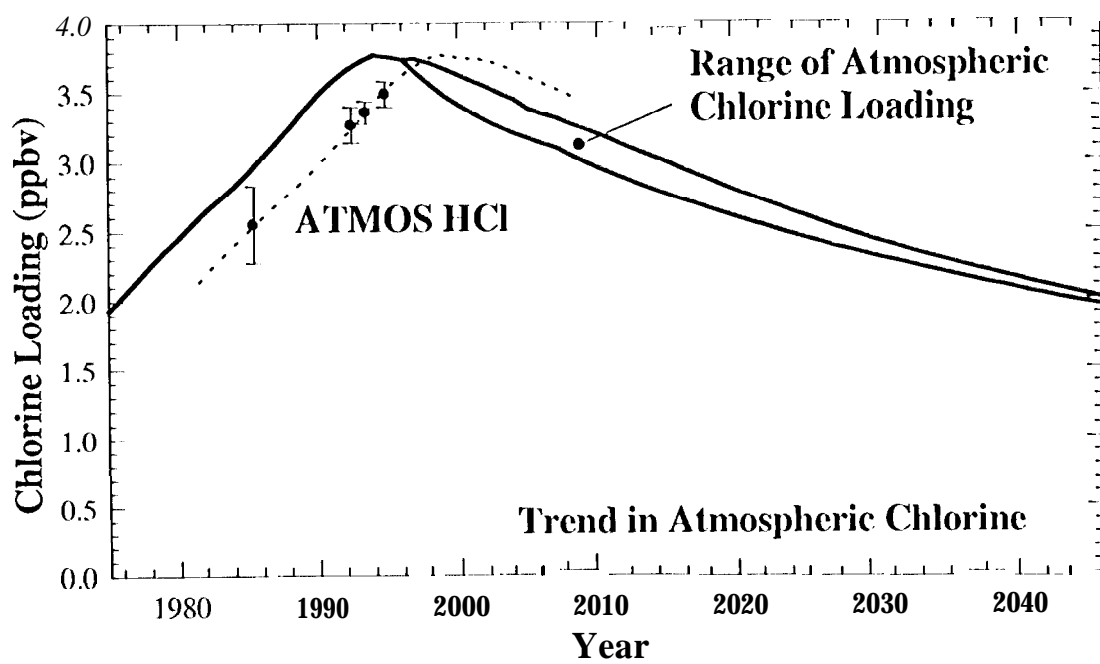


FIGURE 3